

Generalized Coupling Parameter Expansion: Application to Square well and Lennard-Jones fluids

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The coupling parameter expansion in thermodynamic perturbation theory of simple fluids is generalized to include the derivatives of bridge function with respect to coupling parameter. We applied the theory to Square-Well (SW) and Lennard-Jones(LJ) fluids using Sarkisov Bridge function. In both cases, the theory reproduced the radial distribution functions obtained from integral equation theory (IET) and simulations with good accuracy. Also, the method worked in the liquid-vapor coexistence region where the IETs are known to fail. In the case of SW fluids, the use of Carnahan-Starling expression for Helmholtz free energy density of Hard-Sphere reference system has improved the liquid-vapor phase diagram(LVPD) over that obtained from IET with the same bridge function. We also obtained the surface tension for SW fluids of various ranges. Results of present theory and simulations are in good agreement. In the case of LJ fluids, the equation of state obtained from the present method matched with that obtained from IET with negligible deviation. We also obtained LVPD of LJ fluid from virial and energy routes and found that there is slight inconsistency between the two routes. The two applications above lead to following conclusions. In cases where reference system properties are known accurately, the present method gives results which are very much improved over those obtained from the IET with the same bridge function. In cases where reference system data is not available, the method serves as an alternative way of solving the Ornstein-Zernike equation with a given closure relation with the advantage that solution can be obtained throughout the phase diagram with a proper choice of the reference system.

I. INTRODUCTION

Describing accurately the thermodynamics and structure of fluids with short ranged inter-particle potentials has been a long standing problem in liquid state theory. Various methods have been developed to attack the problem. They can be divided into two categories. One category is based on integral equation theory(IET) and the other is based on thermodynamic perturbation theory(TPT) [1]. Methods based on IET take into account correlations between particles and aim at accurate description of structural properties of liquids i.e., the radial distribution function (RDF), direct correlation function (DCF) etc. The IETs involve solving the Ornstein-Zernike equation(OZE) coupled with a closure relation. Thermodynamic properties like internal energy and pressure are obtained as integrals of RDF. But inside the two phase region, most of the closures do not have a solution[2]. Apart from this, the IET method suffers from lack of thermodynamic consistency between the energy, virial and compressibility routes. Various closure relations were proposed to minimize the inconsistency[3]. Also closures with adjustable parameters have been proposed to enforce thermodynamic consistency by adjusting them. The requirement of consistency makes the computations complicated. Despite the improvements, accurate description of thermodynamic and structural properties of simple liquids with narrow potentials is still lacking.

On the other hand, in earlier formulations of TPT, the structure and thermodynamic properties of reference system are assumed to be known and the thermodynamic properties of actual system are obtained as a small perturbation over the reference system. The structure of the reference system and the actual system are assumed to be the same. Within this approach, it was not possible to go beyond second order term in the perturbation series as they require higher order correlation functions[4]. Zhou[5] developed a method in which the Helmholtz free energy of the system is written as a series over coupling parameter ζ . This method requires derivatives of the radial distribution function (RDF) at $\zeta = 0$. Zhou calculated the derivatives using finite-difference method and could obtain terms in the perturbation series up to fifth order[6]. Beyond fifth order, it was difficult to obtain reliable estimates of the derivatives because of numerical complications.

Recently, we attempted to address the problem in a more fundamental way combining the ideas of IET and TPT. We assumed that the RDF and the DCF of a system can be written as Taylor series in coupling parameter ζ at $\zeta = 0$. We showed that the terms in Taylor series of both RDF and DCF (i.e., their derivatives) can be obtained by solving a simple set of equations obtained by differentiating the OZE and the generalized closure. The formula for free energy given by Zhou naturally emerges from our formalism apart from the RDF and DCF of the actual system. Within this approach we were able to obtain DCF, RDF and LVPDs for Square Well (SW) fluids of various ranges up to seventh order. By comparing the LVPDs obtained from third, fifth and seventh order versions of our theory, we concluded that the perturbation series for Helmholtz free energy has practically converged by seventh order. However, the series for RDF and DCF didn't converge for low densities and low temperatures for narrow square well fluids. Also, even though the Helmholtz free energy series has converged, we found that there was significant deviation of the obtained LVPD using seventh order TPT from simulation results for narrow SW fluids. The deviation and slow convergence could be because of two reasons: Firstly, we neglected the derivatives of bridge function *w.r.t.* ζ in our calculations and secondly the error in the bridge function we have chosen for calculation.

Also in our previous work, we were able to obtain the RDF and DCF even inside the LVPD and close to the critical region without any problems of convergence of the iteration scheme even though our numerical scheme is very simple. This raises questions about the existence of the solution to OZE inside the spinodal region. The RDF and DCF in the two-phase region find applications in the density functional theory of fluids [7]. One example is the calculation of surface tension. This calculation requires the direct correlation function in the two phase region. As the IETs doesn't have solution in some part of the LVPD, earlier calculations of surface tension were done using an interpolation formula given by Ebner *et.al.*[8] to obtain $c(r)$ inside the two-phase region. In present paper, we address these issues with application to SW fluids. We use the bridge function proposed by Sarkisov[9] with slight modification for SW wells[11] and include its derivatives *w.r.t.* ζ in the calculation. We calculate the RDFs for SW fluids of range 1.3 and LVPDs for SW fluids of ranges 1.25 and 1.375 using seventh order version of our method. Hard-sphere fluid is taken as reference system and Carnahan-starling[10] expression is used for free energy density of the hard sphere reference system. The RDF and DCF of the reference system are obtained by solving the OZE within the Sarkisov approximation modified for SW wells[11]. Interestingly, we could obtain the RDF and DCF of the SW fluid even inside the spinodal region where the Sarkisov's closure is supposed to have no solution. We calculate the surface tension for SW fluids of ranges 1.25, 1.375 and 1.75 using the expression obtained from the square gradient functional for Helmholtz free energy and compare with simulation results.

As an application of our theory to non-hard sphere reference systems, we apply it to Lennard-Jones (LJ) fluid. We use the Sarkisov bridge function for both reference system and perturbation part. The RDFs, isotherms and LVPD for LJ fluid are obtained and compared with those obtained from IET and simulations wherever available. The paper is organized as follows. In Section II we discuss the method briefly. In Section III we apply the theory to SW fluids and in Section IV to LJ fluids and the results are analyzed. The paper is concluded in Section V.

II. THEORY

Consider a fictitious system at temperature T and density ρ with interaction potential $u(\zeta, r)$ given by

$$u(\zeta, r) = u_{ref}(r) + \zeta u_{pert}(r) \quad (1)$$

ζ is a coupling parameter. When $\zeta = 0$, the fictitious system becomes reference system with interaction potential $u_{ref}(r)$. A non-zero ζ will add a perturbation to $u_{ref}(r)$ as shown in above equation. $\zeta = 1$ corresponds to the potential of the system under consideration. We postulated that the RDF and DCF of the system with potential $u(\zeta, r)$ can be written as a McLaurin series in ζ , that is,

$$c(\zeta, r) = c_0(r) + \zeta \left(\frac{\partial c}{\partial \zeta} \right)_{\zeta=0} + \frac{\zeta^2}{2!} \left(\frac{\partial^2 c}{\partial \zeta^2} \right)_{\zeta=0} + \dots \quad (2)$$

$$g(\zeta, r) = g_0(r) + \zeta \left(\frac{\partial g}{\partial \zeta} \right)_{\zeta=0} + \frac{\zeta^2}{2!} \left(\frac{\partial^2 g}{\partial \zeta^2} \right)_{\zeta=0} + \dots \quad (3)$$

Hereafter we shall denote n^{th} partial derivative of any function $X(\zeta, r)$ w.r.t ζ as $X^{(n)}(\zeta, r)$. With simple arguments, it can be seen that the Taylor series expansion for $c(\zeta, r)$ and $g(\zeta, r)$ w.r.t. ζ exists. This requires to prove that both $c(\zeta, r)$ and $g(\zeta, r)$ are analytic in ζ . Using diagrammatic techniques, DCF in general can be written as follows [1]

$$c(1, 2) = \{ \text{sum of all topologically distinct diagrams that consist of two white 1-circles labelled 1 and 2,} \quad (4) \\ \text{black } \rho^{(1)}\text{-circles and } f_M\text{-bonds and are free of connecting circles} \}$$

Notation and conventions are followed as given in ref.([1]). Where $\rho^{(1)}$ is the single particle density which is equal to density ρ in a homogeneous system. $f_M(1, 2) = e^{-\beta u(1, 2)} - 1$ is the Mayer's function. $u(1, 2)$ is the potential between the particle 1 and particle 2 defined by Eq.(1) (ζ is not shown for notational convenience). $\beta = 1/k_b T$. Clearly, potential $u(1, 2)$ enters the definition of $c(1, 2)$ through the Mayer's function in each term. Separating the reference and perturbation part of the potential in the exponential term of the Mayer's function,

$$f_M(1, 2) = e^{(-\beta(u_{ref}(1, 2)))} e^{(-\beta(\zeta u_{pert}(1, 2)))} - 1 \quad (5)$$

From the above Eq.(5), it can be seen that the Mayer function is analytic in ζ unless $u_{pert}(1, 2)$ has some singularity, as the exponential function is an analytic function. Thus the Mayer's function, which is the first term in the diagrammatic expansion of $c(1, 2)$ can be written as a Taylor series in ζ which is nothing but the series obtained by expanding the exponential containing ζ .

Since the Mayer's function is the basic component in all the diagrams of $c(1, 2)$, all other diagrams also can be expanded in powers of ζ and thus Taylor series expansion exists for each diagram and hence $c(1, 2)$ can be expanded as a Taylor series in ζ . In the case of homogeneous fluid, $c(1, 2)$ depends only on the distance between particles and is written as $c(\zeta, r)$ where r is the distance between the particles.

Also, the diagrammatic expansion for RDF is

$$g(1, 2) = \{ \text{sum of all topologically distinct diagrams that consist of two white 1-circles labelled 1 and 2,} \quad (6) \\ \text{black } \rho^{(1)}\text{-circles and } f_M\text{-bonds and are free of articulation circles} \}$$

From similar arguments given in the case of DCF, it can be seen that $g(\zeta, r)$ is analytic in ζ and a Taylor series expansion exists. Now, with the understanding that a Taylor series expansion exists for both $c(\zeta, r)$ and $g(\zeta, r)$, we proceed to obtain relation between their derivatives as follows: Using the concept of potential of mean force, the radial distribution function can be written as

$$g(\zeta, r) = \exp(\phi(\zeta, r)) \quad (7) \\ \phi(\zeta, r) = -\beta(u_{ref}(r) + \zeta u_{pert}(r)) + y(\zeta, r) + B(\zeta, r)$$

where $y(\zeta, r)$ is the indirect correlation function defined as $h(\zeta, r) - c(\zeta, r)$ and $h(\zeta, r) = g(\zeta, r) - 1$ is the total correlation function of the fictitious fluid. The bridge function $B(\zeta, r)$ is a sum of an infinite series of the "bridge diagrams" [3]. Since $g(\zeta, r)$, and hence $h(\zeta, r)$, as well as $c(\zeta, r)$ are expanded in a series in ζ , the correlation function $y(\zeta, r)$ is also a series in ζ . The n^{th} order coefficient in its series is given by $y^{(n)}(\zeta, r) = h^{(n)}(\zeta, r) - c^{(n)}(\zeta, r)$. Generally, $B(\zeta, r)$ is chosen as a function of $y(\zeta, r)$. Several approximations to $B(\zeta, r)$ in terms of $y(\zeta, r)$ and certain empirical parameters are available [3].

The general expression for n^{th} order derivative of $g(\zeta, r)$ from Eq.(8) is

$$g^{(n)}(\zeta, r) = \sum_{m=0}^{(n-1)} [C_m^{(n-1)}] \phi^{(n-m)}(\zeta, r) g^{(m)}(\zeta, r), \quad n \geq 1 \quad (8)$$

where $[C_m^{(n-1)}]$ is the binomial coefficient. The derivatives $\phi^{(n)}(\zeta, r)$ are given by

$$\phi^{(n)}(\zeta, r) = -\beta u_{pert}(r) \delta_{n,1} + y^{(n)}(\zeta, r) + B^{(n)}(\zeta, r), \quad n \geq 1 \quad (9)$$

where $\delta_{n,1}$ is the Kronecker delta. The derivatives $g^{(n)}(\zeta, r)$ can be computed using Eq.(8) in a recursive manner, using $\phi^{(n)}(\zeta, r)$ either from initial guess or previous iteration. Since

$$c(\zeta, r) = g(\zeta, r) - y(\zeta, r) - 1, \quad (10)$$

its n^{th} order derivative is

$$c^{(n)}(\zeta, r) = g^{(n)}(\zeta, r) - y^{(n)}(\zeta, r), \quad n \geq 1. \quad (11)$$

To get another set of relations between $c^{(n)}(\zeta, r)$ and $y^{(n)}(\zeta, r)$, we consider the Ornstein Zernike Equation (OZE) in Fourier space:

$$h(\zeta, k) = \frac{c(\zeta, k)}{1 - \rho c(\zeta, k)} \quad (12)$$

where $h(\zeta, k)$ and $c(\zeta, k)$ are the Fourier transforms of $h(\zeta, r)$ and $c(\zeta, r)$, respectively.

Also, structure factor $s(\zeta, k)$ is defined as

$$s(\zeta, k) = \frac{1}{1 - \rho c(\zeta, k)} \quad (13)$$

Therefore, using above equation in OZE i.e., Eq.(12) we get

$$s(\zeta, k) = 1 + \rho h(\zeta, k) \quad (14)$$

Now, differentiating Eq.(13) n -times, we get

$$s^{(n)}(\zeta, k) = [s^{(0)}(\zeta, k)] \rho \sum_{m=0}^{(n-1)} [C_m^n] c^{(n-m)}(\zeta, k) s^{(m)}(\zeta, k), \quad n \geq 1 \quad (15)$$

Using Eq.(14) the derivatives of $y(\zeta, k) = h(\zeta, k) - c(\zeta, k)$ are expressed as

$$y^{(n)}(\zeta, k) = \rho^{-1} s^{(n)}(\zeta, k) - c^{(n)}(\zeta, k), \quad n \geq 1 \quad (16)$$

Thus in order to obtain up to N^{th} order term in Taylor series expansion of both $c(1, r)$ and $g(1, r)$, N coupled linear equations in real-space and N coupled linear equations in Fourier space have to be solved simultaneously with $\zeta = 0$.

For example, to obtain Taylor series expansion up to second term, the set of four equations given by

$$c^{(1)}(0, r) = (-\beta u_{pert}(r) + y^{(1)}(0, r) + B^{(1)}(0, r))g(0, r) - y^{(1)}(0, r) \quad (17)$$

$$c^{(2)}(0, r) = (-\beta u_{pert}(r) + y^{(1)}(0, r) + B^{(1)}(0, r))^2 g(0, r) + B^{(2)}(0, r)g(0, r) + y^{(2)}(0, r)(g(0, r) - 1) \quad (18)$$

$$y^{(1)}(0, k) = c^{(1)}(0, k)(s^2(0, k) - 1) \quad (19)$$

$$y^{(2)}(0, k) = c^{(2)}(0, k)(s^2(0, k) - 1) + 2\rho(c^{(1)}(0, k))^2 s^3(0, k) \quad (20)$$

have to be solved (where $g(0, r)$ is $y(0, r) + c(0, r) + 1$).

The CPE for Helmholtz free energy density $f(T, \rho)$ of a homogeneous fluid at a given temperature T is given by [1]

$$f(T, \rho) = f_{ref}(\rho) + \frac{\rho^2}{2} \int_0^1 d\zeta \int d\vec{r} u_{pert}(r) g(\zeta, r) \quad (21)$$

where $f_{ref}(\rho)$ is the free energy density of the reference system. For notational simplicity we do not show temperature dependence of $f(T, \rho)$ explicitly hereafter. Substituting Eq.(3) in Eq.(21) and integrating over ζ , we get

$$f(\rho) = f_{ref}(\rho) + \frac{\rho^2}{2} \int d\vec{r} u_{pert}(r) \left(g_0(r) + \frac{1}{2!} g^{(1)}(0, r) + \frac{1}{3!} g^{(2)}(0, r) + \dots \right) \quad (22)$$

Here we have used the shortened notation for the derivatives $(\partial^n g(r)/\partial \zeta^n)_{\zeta=0}$ which is readily obtained as $y^{(n)}(0, r) + c^{(n)}(0, r)$. Thus the method provides the DCF, RDF as well as the free energy density. The Taylor series of RDF truncated up to second order gives third order CPE for $f(\rho)$.

A. Numerical Procedure

The numerical method is simple and is as explained in our previous paper. However, for the sake of completeness we explain it here. Firstly, it has to be noted that the present method offers the flexibility to use any known quantity of the reference system like $c^{(0)}(0, r) = c_0(r)$, $g^{(0)}(0, r) = g_0(r)$ or the reference system free energy density $f_{ref}(\rho)$. For example, in the case of Hard-Sphere reference system, the Carnahan-Starling expression for $f_{ref}(\rho)$ can be used. Similarly, $g_0(r)$ and $c_0(r)$ obtained from simulations may be used. Alternatively, they can be generated by solving the OZE using some bridge function using the same procedure as outlined below. In such a case, the method amounts to solving the OZE in an alternative way. To compute the derivatives, say, up to n^{th} order, Eq.(11) in real space and Eq.(16) in Fourier space are solved employing an iterative procedure. First of all, we choose guess solutions for $y^{(m)}(0, r)$ (in practice a null solution suffices), for all m in the range $1 \leq m \leq n$, and compute $g^{(m)}(0, r)$, using Eq.(8). Then, $c^{(m)}(0, r)$ are obtained using Eq. (11). Next, their Fourier transforms $c^{(m)}(0, k)$ are computed using an FFT algorithm. Mesh widths in the range 0.01 to 0.001 are found to be adequate. These are employed in Eq.(15) to obtain $s^{(m)}(0, k)$. These functions, when used in Eq.(16), provide $y^{(m)}(0, k)$. Inverse Fourier transformation of it gives $y^{(m)}(0, r)$. This completes the first iteration. However, before starting the next iteration, we employ a linear mixing of the initial and new solutions: $\alpha y^{(m)}(0, r) + (1 - \alpha)y^{(m)}(0, r) \rightarrow y^{(m)}(0, r)$. They are then used in Eq.(11) for the second iteration. The procedure is repeated until the root mean square differences between successive iterates of $y^{(m)}(0, r)$, for all m , are less than a prescribed tolerance. We find that $\alpha = 0.5$ and tolerance of 10^{-8} are adequate to get accurate solutions.

III. APPLICATION TO SQUARE WELL FLUIDS

Seventh order version of above mentioned theory is applied to SW fluids. We use the closure proposed by Sarkisov with slight modification by Mendoub[11].

$$B(\zeta, r) = (1 + 2y^*(\zeta, r))^{1/2} - 1 - y^*(\zeta, r) \quad (23)$$

where

$$\begin{aligned} y^*(\zeta, r) &= y(\zeta, r) + \rho f_M(\sigma^+)/2, \quad r < \sigma \\ &= y(\zeta, r) + \rho f_M(r)/2, \quad r \geq \sigma \end{aligned} \quad (24)$$

and σ is the Hard sphere diameter. We obtained the RDF and DCF of the reference system using the same bridge function by solving the OZE using a similar procedure as explained above.

Reduced units ($\epsilon/k_B = \sigma = 1$, where ϵ is the well depth and σ is hard sphere diameter) are used throughout the paper. In Fig.(1) we compare $g(r)$ obtained using 7th order version of our TPT and that obtained through IET[11] for SW fluid of range 1.3 for densities 0.2 and 0.8 and temperature $T = 1.0$. Clearly, there is negligible difference between results obtained using present method and those obtained from IET. We observed that except for very low temperatures and low densities, results of fifth order and seventh order TPTs have negligible deviation showing that the Taylor series has converged. Also convergence of the iteration scheme is good in the whole phase diagram. $g(r)$ obtained by our method for SW fluid of range 1.25 in the spinodal region at $\rho = 0.4$ and $T = 0.65$ is shown in Fig.(1). Above observations show that the present method can be viewed as an alternative way of solving the OZE. Advantages of solving the OZE using the perturbation method are, firstly solutions to OZE can be obtained inside the spinodal region also where earlier methods fail and secondly a simpler numerical scheme is sufficient throughout the phase diagram. Apart from these, any known information about the reference system can be used to improve the accuracy of the calculations. For example, in the present case we used the Carnahan-Starling expression for Helmholtz free energy density of the reference system. In Fig.(2) and Fig.(3) we give plots of LVPD for SW fluids of ranges 1.375

and 1.25 respectively using seventh order version of TPT. Our results are compared with simulations, those obtained from IET[11] and our previous results using Malihevsky-Labik bridge function neglecting the derivatives of bridge function. Results of the present calculations are very much improved in the liquid part of the LVPD over those of Mendoub. The main reason for this improvement is the use of Carnahan-Starling expression for free energy. Also the present results significantly improved our previous results[12] where we neglected the derivatives of bridge function. Possibility of obtaining $c(r)$ in two phase region opens up applications in density functional theory(DFT) of liquids. One simple application is studying the surface properties of liquids like surface tension etc. We use the $c(r)$ obtained from seventh order version of TPT to obtain surface tension for SW fluids. Formula for surface tension is obtained by Yang et. al. [13] from square-gradient functional for Helmholtz free energy of inhomogeneous fluids. A brief derivation is as follows: The square-gradient approximation for Helmholtz free energy functional of an inhomogeneous liquid occupying volume Ω at temperature T is given by

$$F[\rho(\vec{r})] = \int d\vec{r} \{f(\rho(\vec{r})) + f_g(\rho(\vec{r}))|\nabla\rho(\vec{r})|^2\} \quad (25)$$

where $f(\rho)$ is Helmholtz free energy density of homogeneous liquid. The second term is the effect of inhomogeneity. $\rho(\vec{r})$ is the number density in an infinitesimal volume around \vec{r} . $F[\rho(\vec{r})]$, $f(\rho(\vec{r}))$ and $f_g(\rho(\vec{r}))$ are all functions of T even though the dependence is not shown explicitly.

The coefficient f_g of gradient term also referred as influence parameter is

$$f_g[\rho(\vec{r})] = \frac{1}{12\beta} \int d\vec{r}' r'^2 c[\rho(\vec{r}), r'] \quad (26)$$

We assume that liquid-vapor interface is flat and that z -axis is normal to the interface pointing out into the vapor from the liquid. In such a case, Eq.(27) becomes

$$F[\rho(z)] = A \int dz \{f(\rho(z)) + f_g(\rho(z))\left|\frac{d\rho(z)}{dz}\right|^2\} \quad (27)$$

where A is the surface area. Grand free energy of the system is given as

$$\Gamma[\rho(z)] = F[\rho(z)] - \mu N \quad (28)$$

where μ is the chemical potential of the system and N is the total number of particles

Minimizing Γ w.r.t. ρ we get

$$\frac{d}{dz} \left[f_g(\rho) \left(\frac{d\rho}{dz} \right)^2 \right] = \frac{d\gamma(\rho)}{dz} \quad (29)$$

where $\gamma(\rho)$ is the grand free energy density.

Integrating above Eq.(29) with boundary conditions

$$\rho(z \rightarrow \infty) = \rho_g; \rho(z \rightarrow -\infty) = \rho_l \text{ and } \frac{d\rho(z \rightarrow \pm\infty)}{dz} = 0 \quad (30)$$

gives

$$\frac{d\rho}{dz} = \left[\frac{\gamma(\rho) - \gamma(\rho_l)}{f_g(\rho)} \right]^{1/2} \quad (31)$$

where ρ_l and ρ_g are coexisting liquid and vapor densities for temperature T under consideration. Surface tension S can be calculated using the formula

$$S = 2 \int_{-\infty}^{\infty} f_g(\rho) \left(\frac{d\rho}{dz} \right)^2 dz \quad (32)$$

Using Eq.(31) in above equation gives

$$S = 2 \int_{\rho_g}^{\rho_l} [f_g(\rho)(\gamma(\rho) - \gamma(\rho_l))]^2 d\rho \quad (33)$$

In the above equations $\gamma(\rho_l)$ may be replaced by $\gamma(\rho_g)$ also as both have same value.

Above explained formalism is applied to SW fluids of ranges 1.375, 1.5 and 1.75 with $c(r)$ obtained from seventh order TPT as explained above. Fig.(4) shows $f_g(\rho)$ as a function of ρ for different temperatures for SW fluid of range 1.25. From Fig.(4) it can be seen that $f_g(\rho)$ becomes negative at high densities which is unphysical. This might be an artifact of the approximate bridge function used. However, within the binodal, where f_g is required for the calculation of surface tension(S), it is positive. Surface tensions obtained from our calculation are plotted as a function of T in Fig.(5). Our results compare well with simulations except close to the critical temperatures.

IV. APPLICATION TO LENNARD JONES FLUID

The theoretical formalism explained in section II is general and can be applied to non-hard sphere reference systems also. As an example, we apply the theory to Lennard Jones(LJ) fluid. The Lennard Jones potential is split into reference and perturbation parts according to the Weeks Chandler and Anderson (WCA)[14] method. For this case, we use for $B(\zeta, r)$, the expression proposed by Sarkisov [9] which is same as Eq.(23) with

$$\begin{aligned} y^*(\zeta, r) &= y(\zeta, r) - \rho\beta u(r_m), \quad r < r_m \\ &= y(\zeta, r) - \rho\beta u(r), \quad r \geq r_m \end{aligned} \quad (34)$$

where r_m is the minimum energy point of the Lennard-Jones potential. The reference system $c(r)$ and $g(r)$ are obtained by solving the OZE with the same bridge function. Thus, in effect, we solve the OZE for LJ fluid with the above bridge function using the perturbation method. In Fig.(6), we compare the RDF of LJ fluid obtained from seventh order TPT with simulation results. There is excellent agreement between seventh order TPT and simulation results for the cases shown except for a slight deviation for the case with lowest temperature. In Fig.(7), Equation of State(EOS) of LJ fluid for various temperatures obtained using seventh order TPT is compared with those obtained by solving OZE by Sarkisov[9]. Pressure(P) is obtained using the virial formula given by

$$P = \rho k_B T - \frac{1}{6} \rho^2 \int_0^\infty \frac{du(r)}{dr} g(r) 4\pi r^2 dr \quad (35)$$

Values obtained by our method matched with negligible deviation from those given by Sarkisov. Also, using our method we could obtain the pressure(P) for all density points in the phase diagram as $g(r)$ at any point in the phase diagram could be calculated. This is an advantage of the present method over directly solving the OZE as solution cannot be found inside the two phase region. Again, even close to the critical region, the same numerical procedure was sufficient whereas IETs face numerical convergence problems in this region. In Fig.(8), LVPD of LJ fluid is shown and compared with simulation results. We plotted the LVPDs obtained in two ways. One is obtained by Maxwell construction of pressure isotherm obtained using Eq.(35) which is the so called virial route. This is shown in solid line in Fig.(8). LVPD shown in dashed line in Fig.(8) is obtained using the energy route. It is obtained as follows: Pressure isotherm of the reference fluid is obtained using Eq.(35) with $u_{ref}(r)$. From this, Helmholtz free energy density of the reference fluid is obtained from the formula below

$$f_{ref}(\rho) = \rho k_B T \int_0^\rho \left(\frac{P_{ref}(\rho')}{\rho'^2} - 1 \right) + \rho k_B T \ln(\rho) \quad (36)$$

Once the reference free energy is obtained, method described in section II can be applied to get the free energy density of the required system. The pressure isotherm is obtained by differentiating the Helmholtz free energy *w.r.t.* volume of the system. Maxwell construction is done to get the coexistence points. From the figure, it can be seen that the LVPDs obtained from both the routes differ slightly along the liquid part of coexistence curve. Also, there is some deviation of both LVPDs from the simulation results. This is due to the bridge function used. Even though Sarkisov bridge function is supposed to be quite accurate, there is still some inconsistency between various thermodynamic routes. Imposition of the thermodynamic consistency between various routes as a constraint would solve the problem and may improve the accuracy of the results. This can be done in a straight-forward way within the theory presented in the paper.

V. CONCLUSIONS

In this paper we investigated in detail the coupling parameter expansion of simple fluids. We have generalized our previous version by including the derivatives of the bridge function in the method. The theory has been applied to study square well fluids and Lennard Jones fluids using Sarkisov bridge function.

In the case of SW fluids, we showed that the $g(r)$ obtained from seventh order TPT matches well with that obtained from IET. We noticed that solutions to OZE can be obtained inside the spinodal also where ordinary IETs fail. The LVPDs obtained using the present method improved over those obtained from IET. This is because of usage of accurate parametrization of reference system free energy density which is not possible in IET. Usage of a improved bridge function and including the derivatives of the bridge function also in the coupling parameter expansion improved the LVPDs of SW fluids over our earlier calculations. Possibility of obtaining solutions of OZE in two phase region helped to obtain interfacial properties. We obtained the surface tension of SW fluids of ranges 1.375, 1.5 and 1.75. Agreement with simulation results is found to be quiet good except close to the critical region. As an application to non hard-sphere fluids, we applied the method to Lennard-Jones fluids. In this case also, we found that the seventh order perturbation theory results match with those obtained using IET with the same bridge function. Additionally, we were able to obtain solutions in the spinodal region also where the IET doesn't have solutions. LVPD is obtained through energy and virial routes and compared with simulations.

Thus present method can be viewed as an alternative way of solving the Ornstein Zernike equation with a given closure. The advantages that we noticed in solving the OZE in this way are, firstly, the solution can be obtained in the coexistence region also where earlier methods of solution fail. Secondly, a simple numerical scheme is sufficient and works even in the critical region. Apart from this, the perturbation method allows to choose a reference system whose properties may be known more accurately. Also, the reference system can always be chosen in such a way that its interaction potential $u_{ref}(r)$ is only repulsive and thus doesn't have a liquid vapor coexistence. For such a reference system, any closure would give solution in the entire phase diagram. Since the perturbation method described in the paper confines to obtaining derivatives strictly at $\zeta = 0$, and the n^{th} order derivative depends only on derivatives upto $(n - 1)^{th}$ order, all the derivatives exist once the reference system has a solution throughout the phase diagram. More clearly, the first derivatives of RDF and DCF of the required system depend only on the reference system RDF and DCF. Hence they can be obtained if reference system RDF and DCF are known. Once they are obtained, second derivatives of RDF and DCF can be calculated as they depend only on reference system RDF, DCF and first derivatives of RDF, DCF and so on. Thus the existence of solution of OZE for the actual system depends on the existence of solution of OZE for the reference system which will in general exist if the reference system is chosen to have only repulsive interaction. The convergence of Taylor series expansion is seen to be quiet satisfactory except for very low temperatures and low densities for narrow wells. Thus the accuracy of the present method is limited only by the bridge function used. Implementation of consistency condition in bridge function may improve the accuracy of the present method which is a subject of our future work.

VI. ACKNOWLEDGEMENTS

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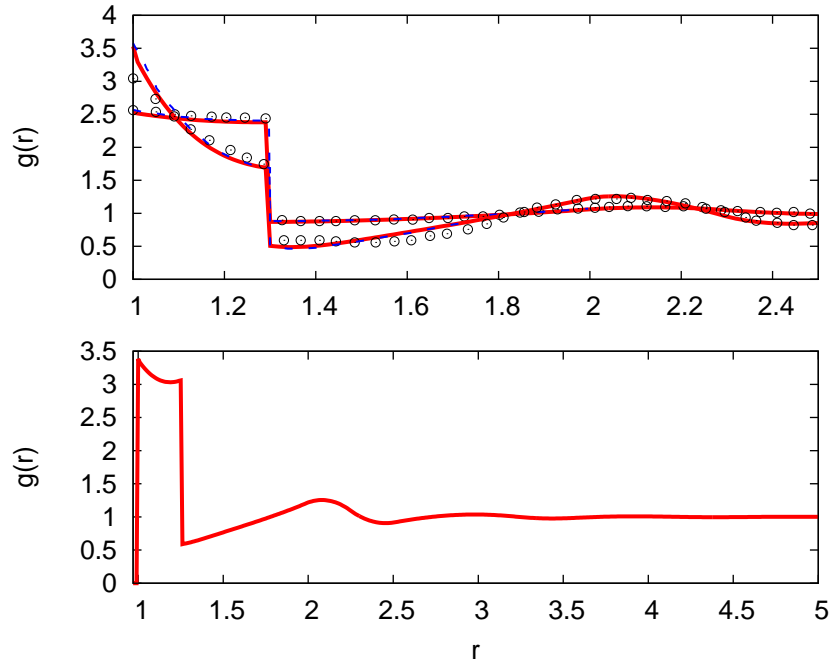


FIG. 1. (Color Online) Top: $g(r)$ for SW fluid of range 1.3 for densities 0.2,0.8 and $T = 1.0$. (Circles: simulation results[15]); (Dashes: IET results [11]); (Solid lines: results from present calculations). Bottom: $g(r)$ for SW fluid of width 1.25, temperature $T = 0.65$ and density 0.4.

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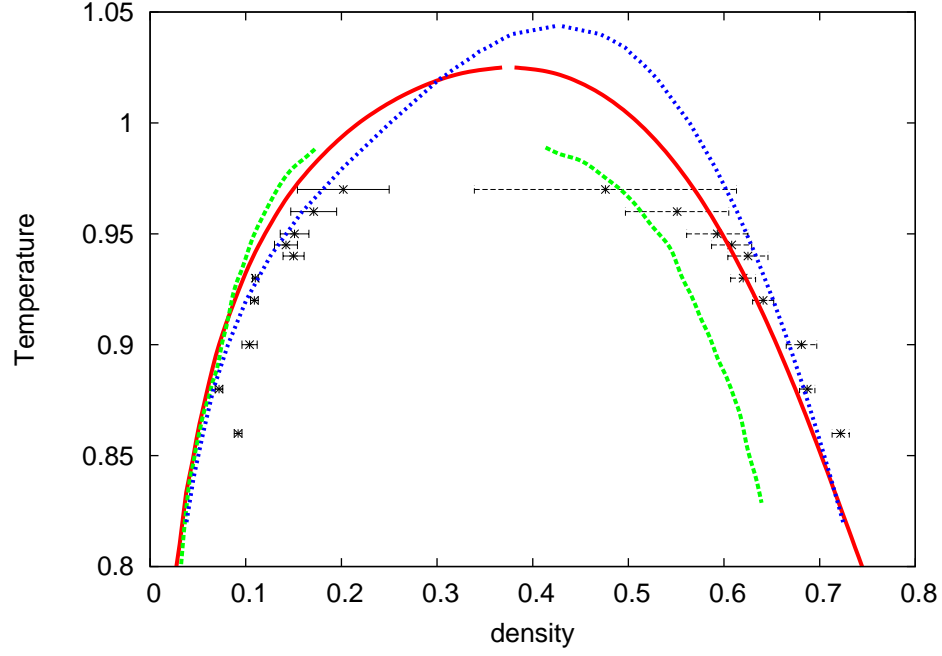


FIG. 2. (Color Online) LVPD of SW fluid of range 1.375. (dotted line: 7th order TPT with Malijevsky Labik bridge function[12]); (solid line: 7th order TPT with Sarkisov $B(r)$ (present work)); (Short dashes IET results with Sarkisov $B(r)$ obtained from Mendoub et. al.[11]); (Squares and stars are simulation results[16, 17]);

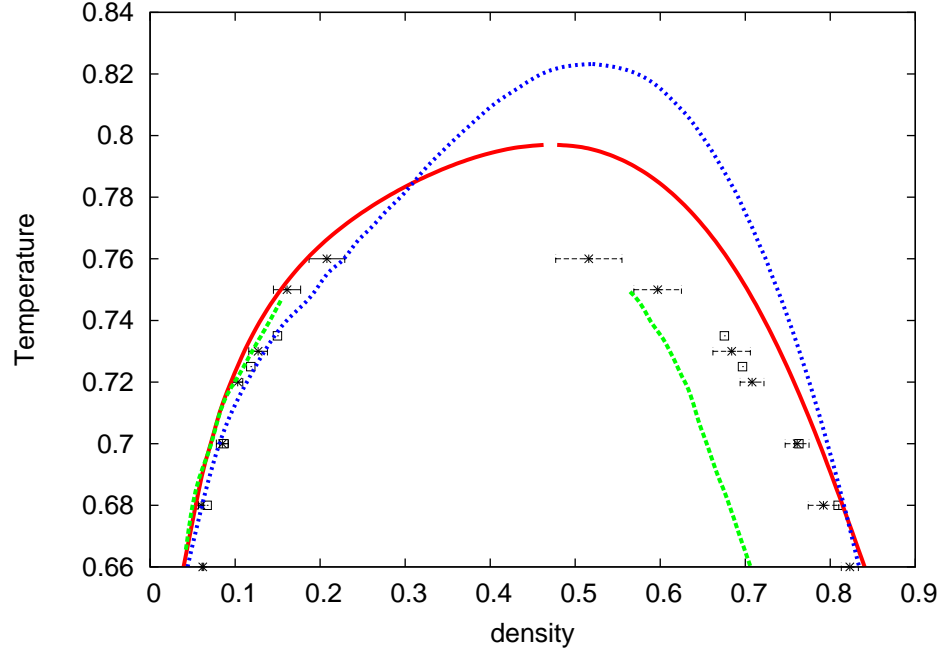


FIG. 3. (Color Online) LVPD of SW fluid of range 1.25. (dotted line: 7th order TPT with Malijevsky Labik bridge function[12]); (solid line: 7th order TPT with Sarkisov $B(r)$ (present work).); (Short dashes IET results with Sarkisov $B(r)$ obtained from Mendoub et. al.); (Squares and stars are simulation results[16, 17]);

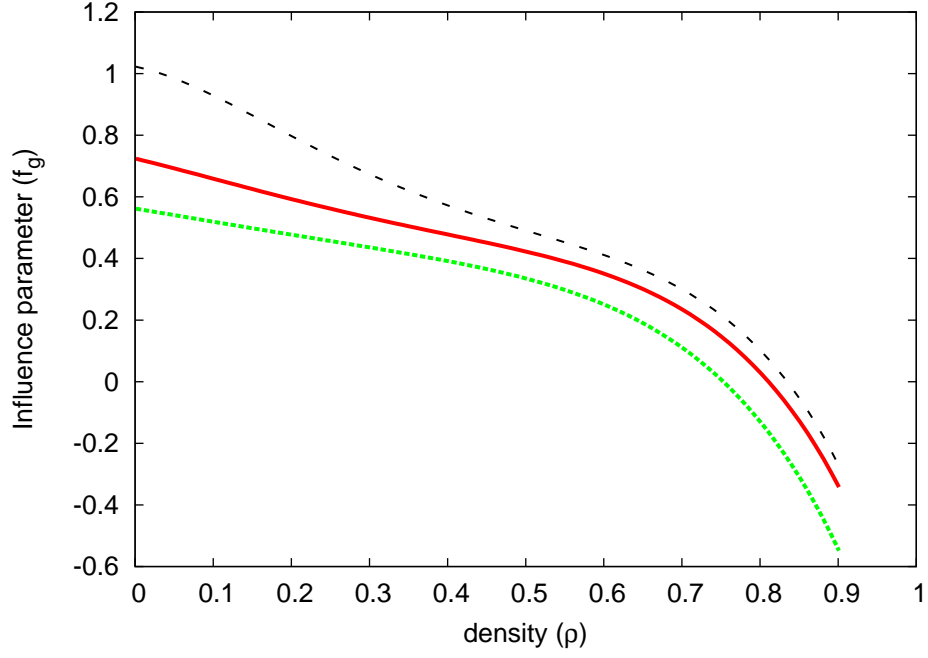


FIG. 4. (Color Online) Coefficient of square gradient functional for SW fluid of range 1.25. Curves from top to bottom are for temperatures $T = 0.6, 0.8$ and 1.0 .

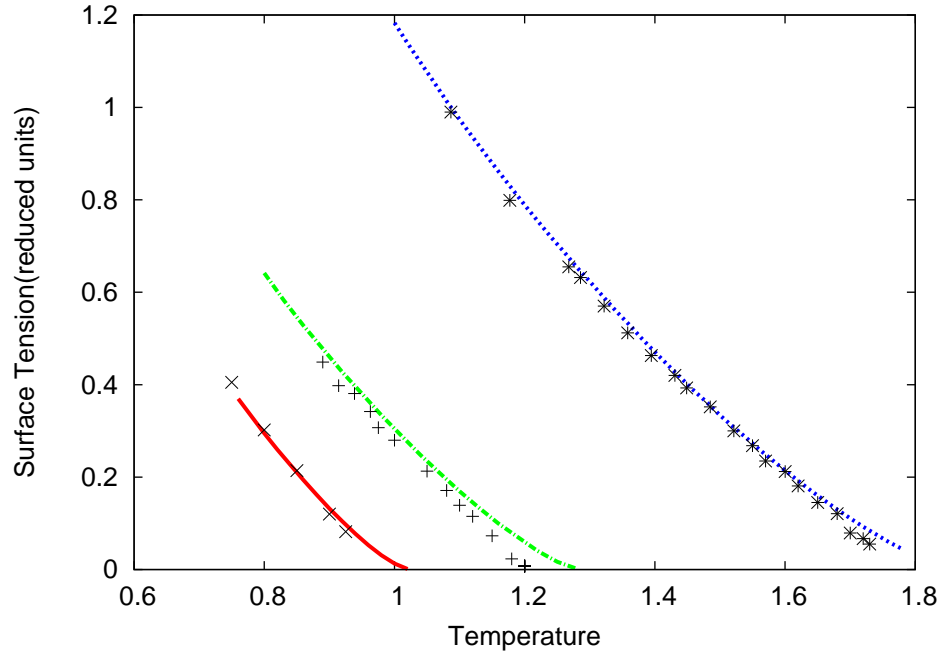


FIG. 5. (Color Online) Surface tension for SW fluids in reduced units. From left to right are for ranges 1.375, 1.5 and 1.75. stars, pluses, crosses are simulation results[18, 19].

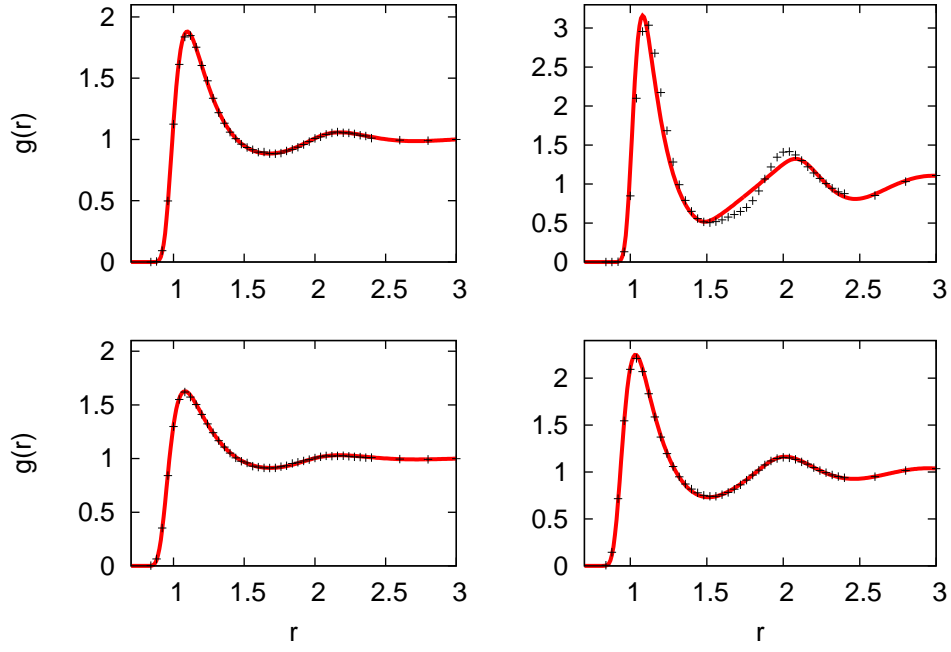


FIG. 6. (Color Online) LJ rdbs for different temperatures and densities obtained using 7th order TPT. (pluses: Simulation results[20]),(Top left: $T = 1.552, \rho = 0.45$),(Bottom left: $T = 2.934, \rho = 0.45$),(Top right: $T = 0.658, \rho = 0.85$),(Bottom right: $T = 2.888, \rho = 0.85$). T and ρ are in reduced units

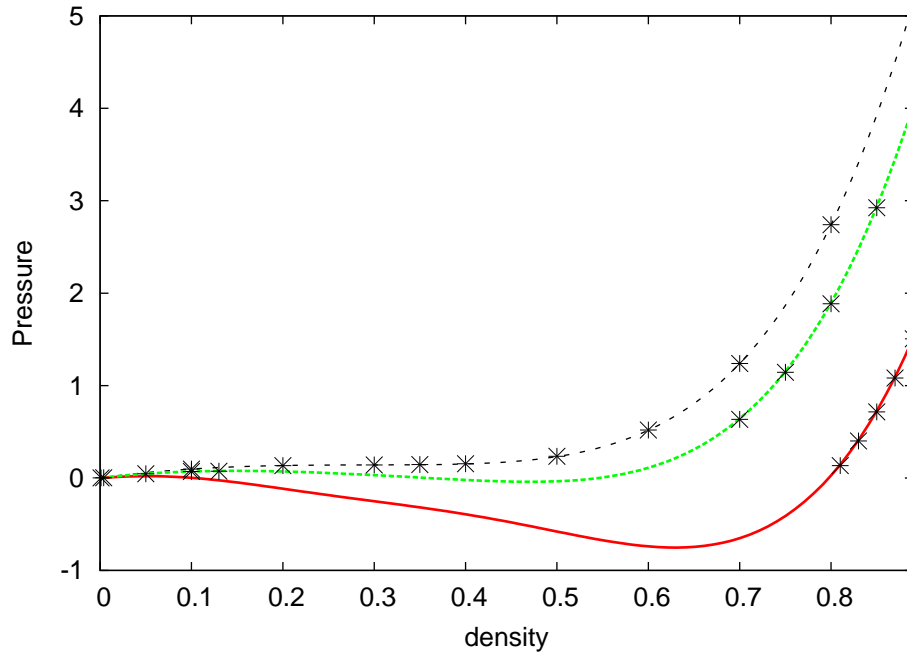


FIG. 7. (Color Online) : EOS of LJ fluid for different temperatures. Stars: Values obtained using IET by Sarkisov[9]. Lines: 7th order TPT results with Sarkisov bridge function. (Solid line: $T = 0.75$),(Dotted line: $T = 1.15$),(Dashes: $T = 1.35$)

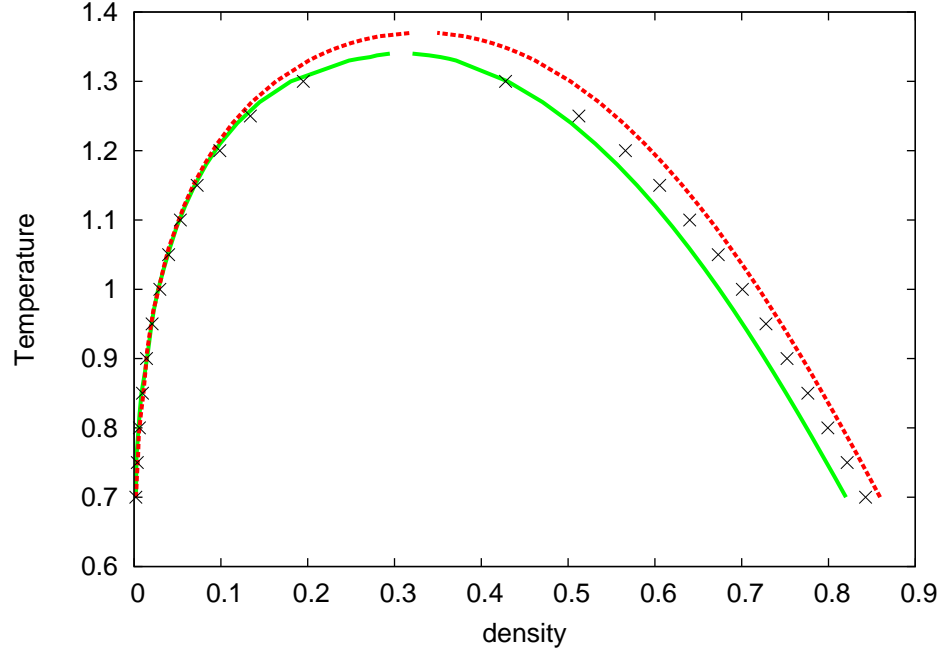


FIG. 8. (Color Online) LVPD of LJ fluid. Dashed line is obtained from EOS calculated using energy route. Solid line is from EOS obtained using virial route. In both cases Sarkisov bridge function and 7th order TPT are used. Crosses are simulation results[21].